



OXIDATION OF CROTONIC ACID WITH CE (IV) PERCHLORATES

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Abstract- The present manuscript deals the kinetics and mechanism of the reaction between crotonic acid and ceric perchlorates. The order of the reaction with respect to Ce (IV) is unity but the rate is dependent on the initial concentration of the Ce (IV). The spectrophotometric investigation has been also carried out which negatived the intermediate complex formation. The main reaction species of Ce (IV) involved in rate determining step was the hydrated uncomplexed ceric ion which at higher initial concentration gets dimerises.

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Introduction

Although the kinetics investigation of various organic compounds with the Ce (IV) ion has been attempted by many authors [1-7] but the oxidation of unsaturated carboxylic acids has yet not been reported. The X-rays diffraction studies have clearly indicated the existence of the cerium (IV) salts as Ce (IV) acetylacetonate [8], Ce (IV) tetrakis(dibenzoylmethane) [9] and Ce (IV) disalicylalpropalenediammine [10] where the coordination number of Ce (IV) is eight. It seems most likely that the sulphate [11] and nitrate salts which are also eight coordinated having one coordination site may be occupied either by the oxygen atom of a single nitrate or the sulphate ion. In solution, the solvent may occupy the coordination sites so that eight coordinate of Ce (IV) is maintained. In past twenty to thirty years a little bit of work had been performed on the kinetics of the oxidation of organic acid by cerium [12-16]. But there is lots of work was remains untouched so far. The present manuscript deals the studies based on kinetics and mechanism of the reaction between crotonic acid and ceric perchlorates.

Experimental

The progress of the reaction was studied by taking the required volume of ceric perchlorate solution along with adjustable quantity of perchloric acid and distilled water in a reaction vessel painted black toward off any photochemical change. The reaction vessel and the crotonic acid in another vessel were kept at constant temperature in a thermostat. The reactants were mixed by pouring in the required amount of crotonic acid. Aliquots (5.00ml of reaction mixture) were withdrawn at different time intervals and poured into the flask containing the slight excess of standard ferrous ammonium sulphate solution. The excess of ferrous ammonium sulphate was titrated against a standard solution of ceric sulphate using ferroin as an indicator. The concentration of ceric perchlorate at various time intervals was determined by the method described by Szaleo [17].

Materials

Ceric perchlorate was prepared [18] from the analytical L.R. quality of B.D.H. ceric ammonium nitrate. Crotonic acid employed was

A.R. grade (KOCH-LIGHT LABORATORY LTD.).The other reagents used were, perchloric acid (Riedel, 60%), sodium perchlorate (Riedel grade), barium perchlorate (E. Merk, Germany), sodium hydroxide A.R. (B.D.H.), ferrous ammonium sulphate A.R. (B.D.H.) and ferroin (E. Merk).

Results and Discussion

Stoichiometric and Product Analysis

A known excess of Ce (IV)-perchlorate and a fixed amount of crotonic acid were allowed to react completely and after three months the unchanged Ce(IV) was estimated volumetrically. The stoichiometric ratios are given in Table-1.

Table-1 Stoichiometric and Product Analysis

[Crotonic acid] X 10 ³ M	[Ceric perchlorate] X 10 ² N	[Ce(IV)]/[Crotonic acid]
1.00	1.67	11.234
1.00	2.00	10.987
1.00	2.50	11.474
Average value of equivalents = 11.232		

Temperature = 30°C

The identification of product was carried out by ascending type of paper-chromatography using n-butanol saturated with ammonia as solvent system and bromophenol blue as spot revealing agents. Spots having R_f values 0.61 and 0.49 characterizes the presence of acetic acid and formic acid.

The kinetic measurement have shown that in a given run the rate of disappearance of Ce(IV) follows a first order rate expression and the value of first order rate constant k₁decreases with the increase in the initial concentration of Ce(IV).

Table-2 Effect of changing Ce (IV) concentration on the rate of perchlorate oxidation of crotonic acid

[Ceric perchlorate] X 10 ³ M	6.67	5.00	4.00	2.86	2.00	1.54	1.25
k ₁ X10 ⁴ sec ⁻¹	0.499	0.633	0.685	0.799	1.141	1.279	1.559

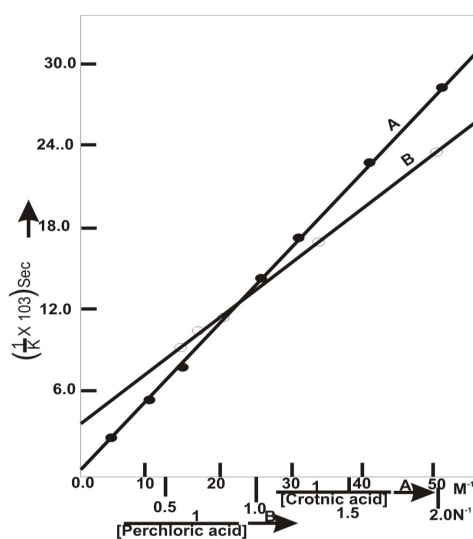


Fig. 1- Plot A (●) shows the variation of inverse rate with crotonic acid concentration in 1N-HClO₄ and [ce(clo₄)₄] = 4.00X10⁻³N.

Temperature = 50°C; [Crotonic acid] = 4.00 x10²M and [Perchloric acid] = 1.00N

In Plot (○), the inverse rate is plotted against the inverse perchloric acid concentration; [Crotonic acid] = 4.00X10⁻²M, [ce(clo₄)₄]

The order of the reaction with respect to crotonic acid has been found to be unity (Table-3). The plot of 1/[crotonic acid] against 1/k₁ is a straight line passing through the origin (Figure-1).

Table-3 Rate dependence on the changing concentration of crotonic acid

[Crotonic acid] X 10 ² M	20.00	10.00	6.67	4.00	3.33	2.50	2.00
k ₁ X10 ⁴ sec ⁻¹	3.951	1.919	1.296	0.685	0.558	0.431	0.354
k ₁ X10 ³ / [crotonic acid]	1.976	1.919	1.943	1.712	1.676	1.724	1.770

Temperature = 50°C; [Ceric perchlorate] = 4.00 X 10⁻³N and [Perchloric acid] = 1.00N

The effect of addition of perchloric acid increases the value of rate constant k₁ and the plot 1/k₁ against 1/[perchloric acid] has been found to be a straight line cutting an intercept from the ordinate (Figure -1). The addition of sodium perchlorate and barium perchlorate to the reaction mixture, do not produce any appreciable change in the rate of reaction (Table-4 and 5).

Table-4 Effect of addition of sodium perchlorate on the rate of reaction

[NaClO ₄] X N	0.00	0.25	0.50	0.75	1.00	1.25	1.50
k ₁ X10 ⁴ sec ⁻¹	0.685	0.691	0.713	0.758	0.796	0.785	0.815

Temperature = 50°C; [Crotonic acid] = 4.00 X 10⁻²M; [Ceric perchlorate] = 4.00X 10⁻³N; [Perchloric acid] = 1.00N

Table-5 Effect of addition of barium perchlorate on the rate of reaction

[Ba(ClO ₄) ₂] (MX10)	0.00	1.00	2.00	3.00	5.00
k ₁ X10 ⁴ sec ⁻¹	0.685	0.682	0.673	0.700	0.752

Temperature = 50°C; [Crotonic acid] = 4.00 X 10⁻²M; [Ceric perchlorate] = 4.00X 10⁻³N; [Perchloric acid] = 1.00N

The value of first order rate constant at different temperatures and the activation parameters are produced in Table 6 and 7 respectively.

Table-6 Effect of variation of temperature on the reaction velocity

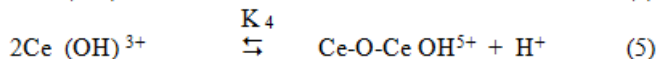
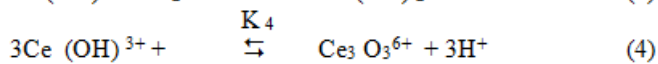
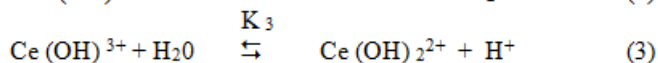
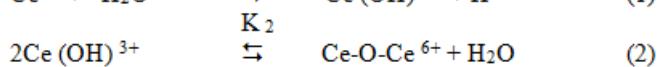
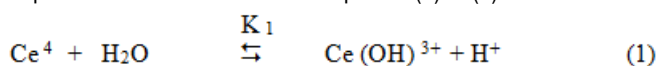
Temperature °C	45	50	55	60
k ₁ X10 ⁴ sec ⁻¹	0.478	0.685	1.262	2.214

[Crotonic acid] = 4.00 X 10⁻²M; [Ceric perchlorate] = 4.00X 10⁻³N; [Perchloric acid] = 1.00N

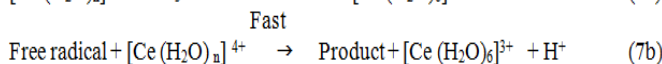
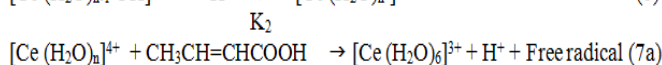
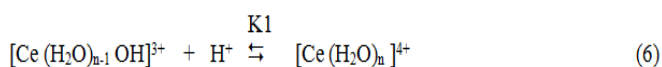
Table-7 Activation parameters at Temperature 50°C

Energy of activation (ΔE) k.cal./mol	Entropy of activation (ΔS^\ddagger) e.u.	Free Energy of activation (ΔG) k.cal./mol
24.03	1.03	23.69

In perchloric acid Ce (IV) does not appear to form stable complexes with perchlorate ion but exists as Ce^{4+} , $Ce(OH)^{3+}$, $Ce-O-Ce^{6+}$ and $Ce(OH)_2^{2+}$ [19-25]. Wiberg and Ford [26] have studied the equilibrium among the Ce (IV) species in aqueous acetic acid and have reported that principal equilibrium is between monomeric and trimeric species with the dimer being relatively unimportant. The various hydrolytic equilibrium of the Ce (IV) species, in perchloric acid is illustrated in equation (1) to (5).



The value of various hydrolytic constants for the equilibria given above, have been reported. However, the dependence of the existence of various species has not been clearly mentioned in the literature but the kinetic and spectrophotometric studies carried out by us suggest that the degree of association of ceric perchlorate in the perchloric acid medium depends on the initial concentration of ceric perchlorate and pH of the solution. Spectrophotometric studies in the U.V. range indicates that the absorbance in the range of $211 \pm 5 \text{ m}\mu$ falls 1.11 to 0.55 when the initial concentration of Ce (IV) is increased from $0.62 \times 10^{-3} \text{ N}$ to $6.67 \times 10^{-3} \text{ N}$. This signifies that at higher concentration the number of absorbing molecules decreases resulting into the formation of polymeric species. The predominant Ce(IV) species at lower concentration is $Ce(OH)^{3+}$. The kinetic observation in Table 2, also indicates that an increasing the concentration of Ce(IV) – perchlorate, the value of k_1 decreases, which also suggested the formation of dimeric species at higher concentration because the behaviour is analogous to that observed in the oxidation of aldehydes [27] and alcohols by chromic acid [28]. This fact has not been reported so far in the kinetic studies of the oxidation of organic compounds by Ce (IV)-perchlorate. The spectrophotometric studies do not give any indication for the intermediate complex formation between Ce (IV) and the crotonic acid. The studies were carried out on PERKIN ELMER Spectrophotometer model-202. Considering the catalytic behavior of $[H^+]$ on the rate of reaction, the reactive species would be the unhydrolysed Ce (IV) species $[Ce(H_2O)_n]^{4+}$. The mechanism of the oxidation is visualized as below.



In this case also, we postulate the C-H bond fission for the electron transfer the eq. (7a) which we assume to be the rate determining step. The oxidation of free radical by $[Ce(H_2O)_n]^{4+}$ which is a fast process produces the product on further fragmentation through C-C bond fission⁴. On the basis of the rate dependence of the reaction with respect to Ce (IV), we can write;

$$-d/dt [Ce(IV)] = k_1 [Ce(IV)]_{\tau} \quad (8)$$

Where $[Ce(IV)]_{\tau}$ indicates the total concentration of Ce (IV) in the reaction and k_1 is the observed velocity constant. The value of $[Ce(IV)]_{\tau} = [Ce(H_2O)_n]^{4+} + [Ce(H_2O)_{n-1}OH]^{3+}$. Thus,

$$k_1 = \frac{k_2 K_1 [H^+][\text{Crotonic acid}]}{1 + K_1 [H^+]} \quad (9)$$

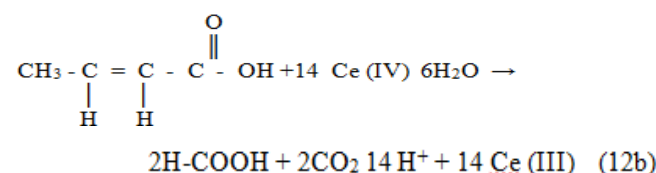
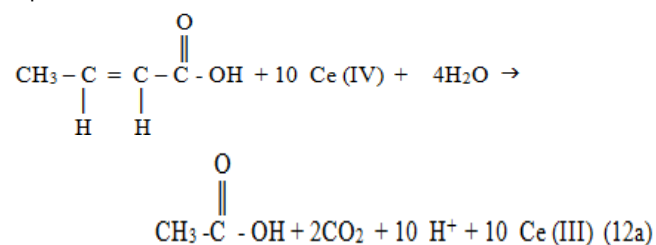
The expression based on the postulated mechanism explains the observed facts that the order is unity with respect to crotonic acid and cerium (IV) and the plot of $1/k_1$ against $1/[HClO_4]$, will be straight line cutting an intercept from the ordinate as shown below;

$$\frac{1}{k_1} = \frac{1}{k_2 K_1 [H^+][\text{Crotonic acid}]} + \frac{1}{k_2 [\text{Crotonic acid}]} \quad (10)$$

This also explains the insignificant effect of the addition of salt to the reaction mixture. The nature of the verification of the k_1 with the initial concentration of Ce (IV) can also be explained because at higher concentration the dimerisation of hydrolysed species takes place and the rate expression will be modified following the appearance of dimeric species at the cost of hydrolysed species. On higher concentration,

$$[Ce(IV)]_{\tau} = [Ce(H_2O)_n]^{4+} + [Ce(H_2O)_{n-1}(OH)]^{3+} + Ce-O-Ce^{6+} \quad (11)$$

And thus, we see that the value of k_1 will be reduced at higher concentration. In the oxidation of crotonic acid, the value of equivalents is found to be 11.232 after a sufficiently long time and thus the reaction can be shown to proceed in two different ways (12a) and (12b) giving rise to the products acetic and formic acid. The reaction precedes 30% through equation 12a and 70% through equation 12b.



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